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(54) Purifying waste gas from fertiliser production

(57) In a process and an apparatus for the joint purification in a wash column (VII) by means of a washing liquid (5) of the waste gases (1,3) and/or vapors (2) formed in the production of inorganic fertilizers, the waste gases (1,2,3) introduced into the wash column are sprayed with a wash liquid (11) after their entry into the lower part of the wash column. The column is typically a filled column with waste gas distribution elements disposed below the filler and spray nozzles near the distributors.

FIG.1

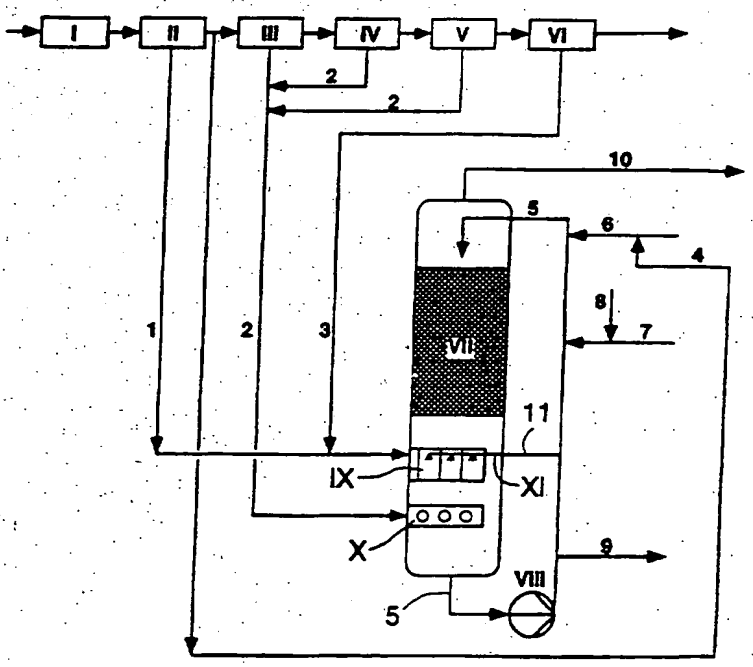

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FIG.1

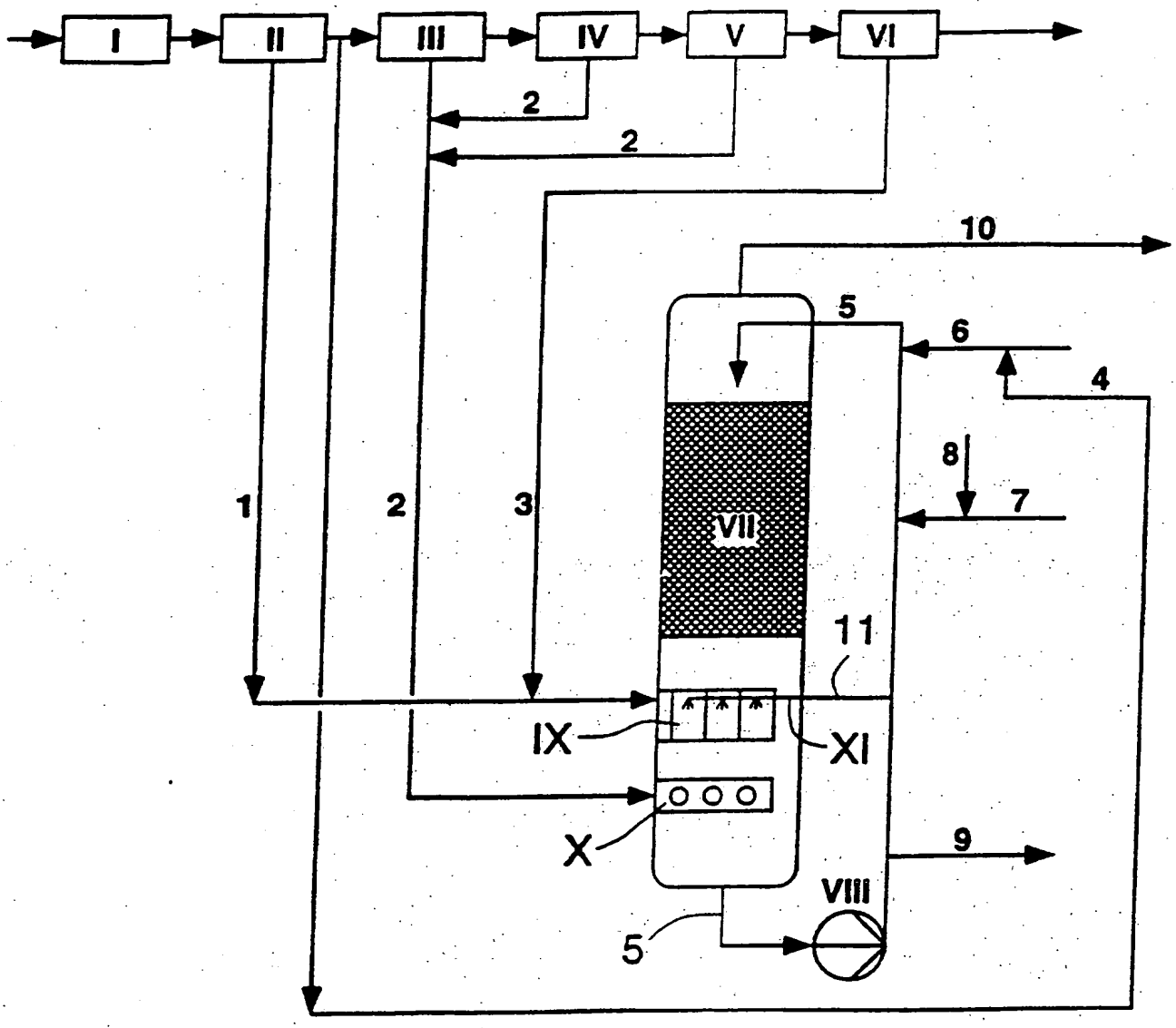


FIG.2

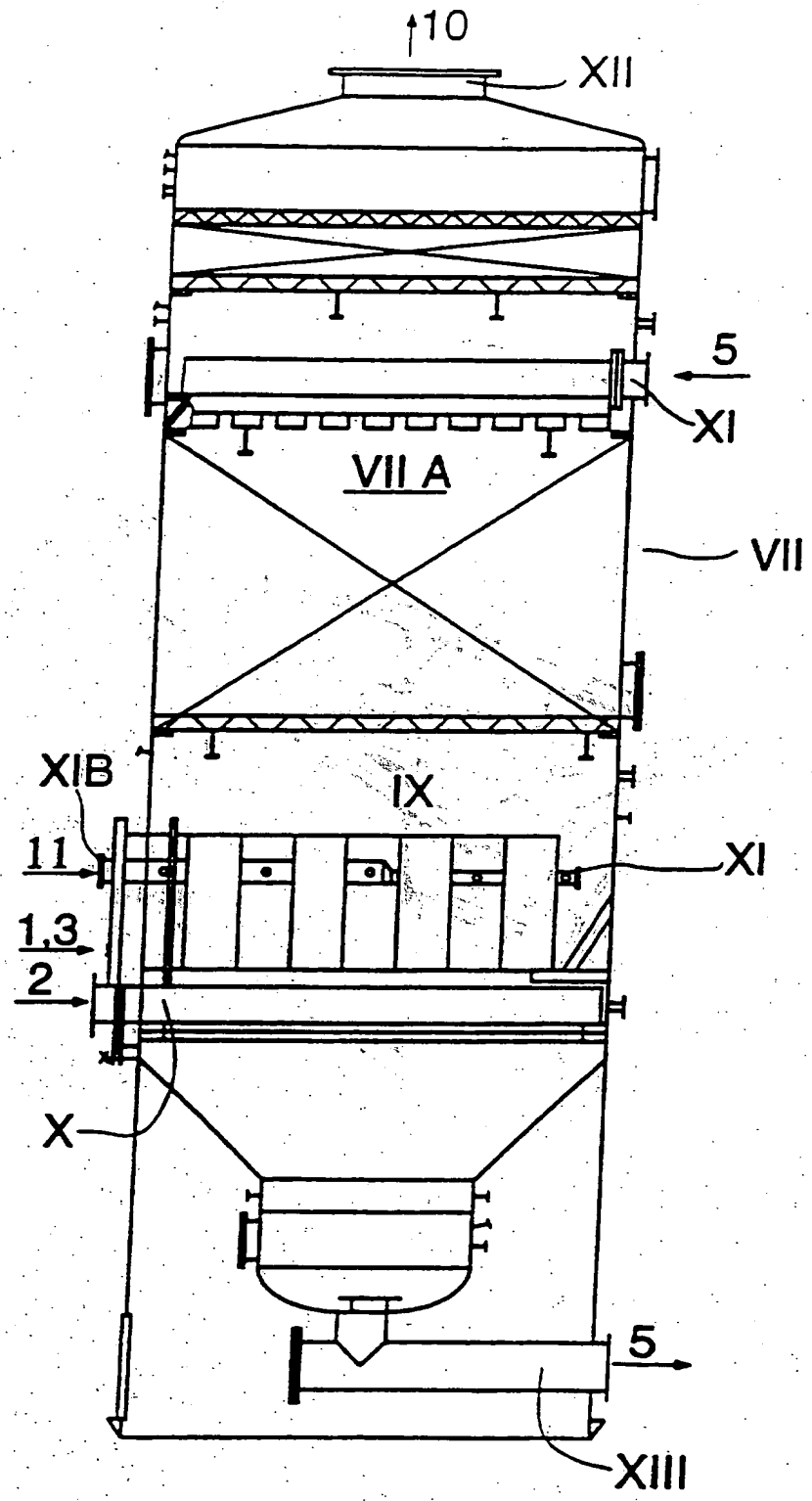
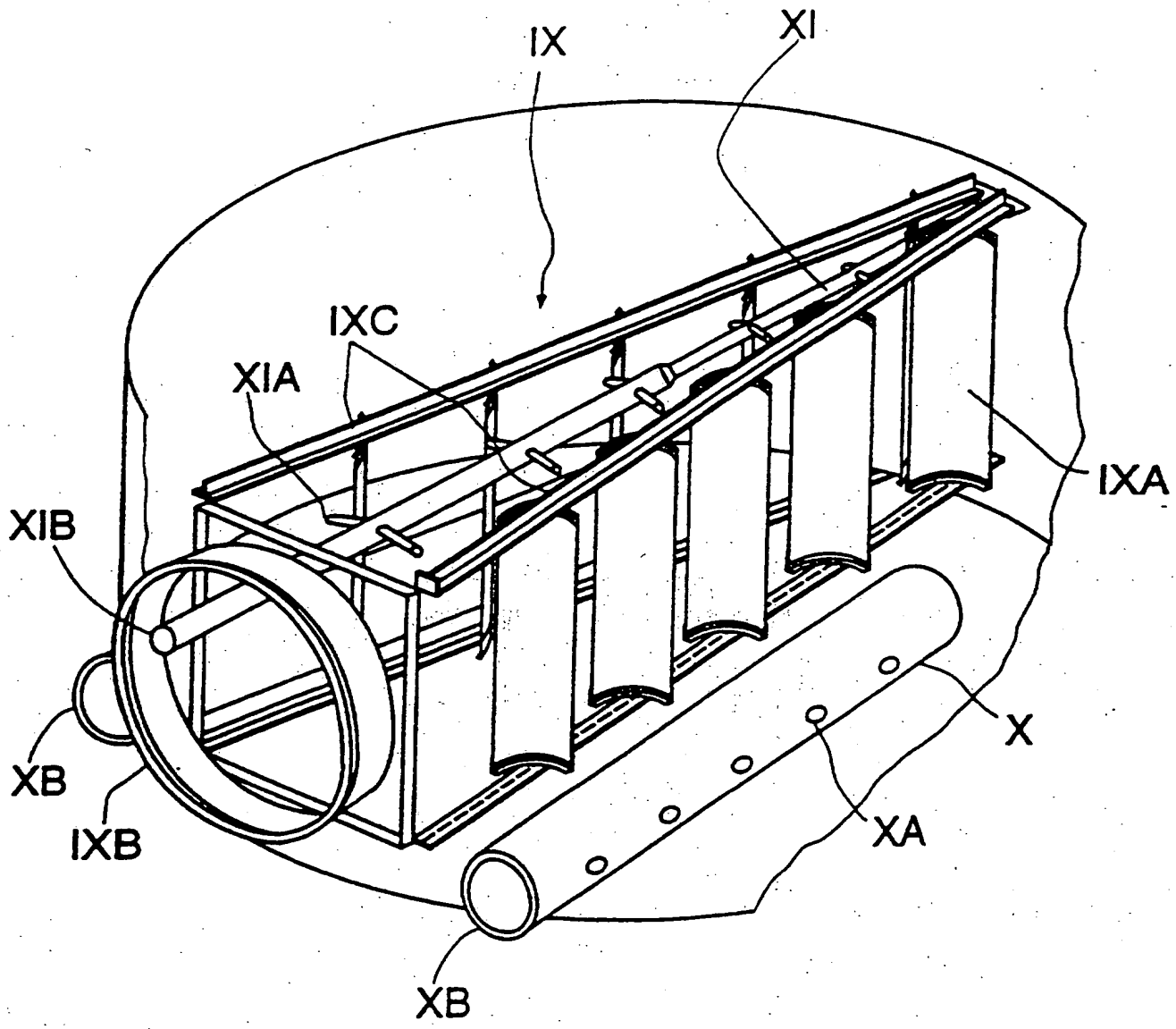


FIG.3



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Purification of the waste gases formed in the production of inorganic fertilizers

The invention relates to a process and an apparatus for the joint purification of the waste gases and/or vapors formed in the production of inorganic fertilizers.

Processes for the production of inorganic fertilizers such as nitrophosphate or nitrophosphate-potassium fertilizers (NP or NPK fertilizers) in general have the following sequential process steps:

- Digestion: The dissolution of the solid raw materials (crude phosphate, diammonium phosphate, monoammonium phosphate, etc.) in mineral acids and removal of insoluble constituents
- Transformation: Specific crystallization of undesired constituents
- Neutralization: Neutralization of the acidic solution with NH_3
- Evaporation: Concentration of the solution, also described as a mash, by evaporation of water
- Mixing with potash: Metering-in of potash and other salts to adjust the formula
- Granulation and drying: Shaping of the mash into granules and residual water removal by means of combustion gases/hot air.

When carrying out these process steps, waste gases and vapors occur in different amounts and with different contents of nitric oxides (NO_x), ammonia (NH_3), water vapor, hydrogen fluoride (HF), silicon tetrafluoride (SiF_4) and solid dusts (alkali metal and alkaline earth metal nitrates, sulfates, phosphates, fluorides and mixed salts) depending on the raw materials employed and the final formula of the inorganic fertilizer to be produced.

According to the existing legal regulations, the waste gases and the vapors must be treated before release to the environment in order to reduce the content of substances contained. A number of processes for this have already been disclosed.

Thus EP-A 0 562 328 describes a process for the simultaneous treatment of collected waste gases and vapors from neutralization, evaporation, mixing with potash, granulation and drying in a single-stage wash column with fittings having separatory activity. The waste gases are purified there, and at the same time by means of the heat content of the waste gases sufficient water is evaporated such that a large part of the harmful substances and solids contained in the waste gases is precipitated in the wash solution and there lead by reaction with one another, by precipitation and crystallization to insoluble sediments and baked-on materials in the liquid distributor of the recirculating wash solution and in the fittings having separatory activity (eg. fillings and packings of filling materials). In particular, in the known processes for the purification of dry, dust-laden waste gases, which are formed in the production of inorganic fertilizers, the problem of the deposition of dust at the gas entry, on the gas distributor and on the surrounding fittings of the column, in particular on the bottom of the packing, always occurs in the waste gas purification columns. This results in significantly reduced

service lives with frequent operational breakdowns. Such breakdowns can only be avoided by regular shutting down and cleaning to eliminate the deposits.

SU-A-360 960 discloses that in a scrubber for the separation of dust from waste gases, which operates using foam, the entering dry, dust-containing gas is humidified by atomization of water into small droplets underneath the foam layer. This has the disadvantage that water additionally passes into the wash solution. This counteracts a desired concentration, which in particular with the process described above is an essential feature.

It is therefore an object of the present invention to reduce the deposits in the area of the gas entry. Additionally, even in the case of peak loadings due to operating fluctuations, the emission of harmful substances should be reliably prevented.

This object is achieved by a process for the joint purification in a wash column by means of a washing liquid of the waste gases and/or vapors formed in the production of inorganic fertilizers. The inventive process comprises spraying the waste gases introduced into the wash column with a liquid after their entry into the lower part of the wash column.

According to a particularly advantageous embodiment of the invention, this liquid consists at least partially of the washing liquid employed in the wash column. The amount of the sprayed liquid is preferably selected such that the entering gas stream is completely sprayed. In this process, at least one part of the sprayed liquid is to be directed against the distributor elements of the distributor system for the waste gases. The

spraying is preferably carried out by nozzles which are arranged in the distributor system for the waste gases in the wash column. Contrary to the view represented in SU-A-360 960, the droplets of the spray liquid do not have to be produced in specifically fine form. It was found that simple nozzles (droplet spectrum, according to type, from 0.1 mm to 5 mm) are sufficient. In the case of separate supply of different waste gas streams of different moisture contents, the spraying is directed into the gas stream having the lowest content of water vapor.

The mode of action of the process according to the invention is that the distributor element for the entering gas is sprayed permanently to prevent deposits. At the same time, the entering gas and the dusts contained are moistened, and the dusts are absorbed by the washing liquid and cannot be deposited on the fittings. Additionally, this additional intensive contact between entering gas and wash solution represents an additional washing step in the case of peak loadings, by which unpermissible emissions are prevented with great effectiveness. Finally, drying of the fittings in the column by superheated air is reliably avoided.

A particular advantage is the use of the wash solution present in the wash column as an absorption medium. By this means, this wash column is virtually equipped with an additional washing stage. A cost-intensive oversizing of the apparatus to trap peak loadings is therefore not necessary.

Further details and advantages of the invention can be taken from the processes described in the following with the aid of the working example shown in the drawing and the apparatus shown. The waste gases to be purified here are supplied in two separate streams.

Fig. 1 shows a scheme of the process according to the invention in block form;

Fig. 2 shows a schematic representation of the wash column employed for carrying out the process, partly in section;

Fig. 3 shows a perspective cross-section through the lower part of the wash column shown in Fig. 2.

In the process scheme shown in Fig. 1, the known sequential process steps mentioned at the outset are shown in block form and provided with Roman reference symbols. In these stages, the following process steps take place:

I. Digestion: Here the solid raw materials (crude phosphate, diammonium phosphate, monoammonium phosphate, etc.) are dissolved in nitric acid, and the insoluble constituents are removed.

II. Transformation: Calcium nitrate tetrahydrate is removed here by specific crystallization. An acidic phosphate solution is formed in this process which essentially consists of a mixture of nitric and phosphoric acid.

III. Neutralization: In this stage the acidic, enriched phosphate solution is neutralized with ammonia. Here water evaporates due to the heat of reaction.

IV. Evaporation: The solution (mash) is concentrated in this stage by further evaporation of water.

V. Mixing with potash: Potassium and other salts are metered in here to adjust the final formula of the product to be produced.

VI. Granulation and drying: In this stage, shaping of the mash into granules and residual water removal take place by means of hot air.

From this sequence of process stages, individual gas streams are formed which are supplied to the lower region of a wash column VII provided

with fittings. The wash column VII can be designed as a packed column. It can also be equipped in a known manner with packings or plates. The branched streams are specifically the streams designated by Arabic numerals 1, 2 and 3. The waste gas formed in the transformation in step II, which essentially contains NO_x and fluorides as harmful substances, is supplied through line 1 to a gas distributor IX arranged under the fittings of the wash column VII. Together with the gas led into the gas distributor IX through line 1, the waste gas from the granulation and drying (VI) is also supplied to this through line 3. From the neutralization (III), the evaporation (IV) and from mixing with potash (V), vapors and fumes are led off through the lines 2 and supplied to a distributor X lying underneath the gas distributor IX. The water vapor-containing waste gases supplied to the distributor X essentially contain NH_3 and fluorides. Both distributors are described in detail later with the aid of Figures 2 and 3. It is also possible to lead all waste gas streams, ie. the streams flowing through the lines 1, 2 and 3, jointly into the wash column VII.

The bottom liquid formed in the wash column VII is drawn off through a line 5 and partially fed back into the upper part of the wash column VII by means of a recirculating pump VIII. One part of the bottom liquid drawn off through line 5 is supplied according to the invention through line 11 to a spray system XI, which in this working example is arranged inside the gas distributor IX. Details of this are explained in greater detail with the aid of Fig. 2 and 3. From the wash suspension led through line 5, which also contains undissolved solids, concentrated wash suspension is led out through line 9 and fed back into the production process of the inorganic fertilizer. To compensate for water losses and to compensate for the concentrated wash suspension drawn off through line 9, process and/or rinsing waters are supplied through line 7. Ammonia or

nitric acid can be supplied to these through line 8 in order to adjust the pH of the water supplied through line 7 to the pH of the circulation suspension in line 5. To adjust the pH and/or the phosphate concentration of the wash solution circulated in line 5, it is possible through line 6 to add nitric acid or acidic phosphate solution, which can be drawn off through line 4 between the stages transformation (II) and neutralization (III). If necessary, phosphoric acid can also be supplied. The purified waste gas is drawn off through line 10.

The wash column VII represented schematically in Fig. 1 will now be explained in greater detail with the aid of Fig. 2.

This wash column VII is essentially a conventional wash column of cylindrical structural design, in whose upper part are arranged fittings VIIA, preferably packing materials. A first distributor XI for the washing liquid supplied through line 5 is provided above these. Above the flange XII, the column VII is connected to the waste gas line 10. Its collecting tube XIII arranged in the lower part is connected via the line 5 with the recirculating pump VIII.

Essential to the invention is - as a second distributor - the spray system XI provided here in the gas distributor IX and arranged below the fittings VIIA, whose details are described below with the aid of Fig. 3. Under this is arranged a distributor X for the vapors and fumes.

The distributor IX is in this working example a vane-type gas distributor which has impact surfaces IXA against which the collective gas stream flowing in through the flange-shaped opening IXB flows and is distributed. At the same time, this gas stream is exposed to the washing liquid flowing down through the fittings VIIA, whereby impurities are dis-

solved and dusts are rinsed down. The vane-shaped impact surfaces IXA are held in fixed position in struts IXC, which in the working example run conically to one another. The angle of the impact surfaces in relation to the gas stream flowing in through the opening IXB is fixed as a function of its amount and velocity. In the present working example, within this vane-type gas distributor is arranged the spray system 11 according to the invention. This consists essentially of a pipeline XIB, which at one end is connected to the line XI and which at the other end is closed after a tapering of the cross-section. Diagonally to the axial direction of this tube XIB, branches XIA are provided which are equipped with drillings or spray nozzles which point downwards.

Below the vane-type gas distributor IX is arranged a tubular distributor X, which is equipped with drillings XA. In the working example, the gas distributor X consists of two tubes led parallel to the gas distributor, through whose supply openings XB is supplied the collective gas stream 2 which contains the waste gases and/or vapors having a high water content and high content of ammonia. The drillings XA are arranged such that they are preferably directed outwardly diagonally to the longitudinal axis of the wash column. The distributor for gases having a high water and NH_3 content can also be of nozzle-like design, it being possible to provide one or more nozzles. The axis of the jet direction of these nozzles preferably runs at right angles to the axis of the wash column.

In a process operating according to the scheme described in Fig. 1 with a column according to Fig. 2 and 3, practice relevant results were achieved. The wash solution used was process rinsing water mixed with NH_3, in which the adjustment of the pH was carried out using 60% strength aqueous HNO_3. In this process, the gases 1 and 3 together form as "dry waste gases" the further collective waste gas stream which is

characterized by a low water vapor content and low ammonia content.

The gas 1 additionally contains a high content of NO_x. This collective waste gas stream is fed into the wash column VII via the vane-type gas distributor IX. The gas 2, which has a high water vapor content and high ammonia content and which can be described as "moist waste gas", is fed into the wash column VII via the tubular distributor X provided with drillings XA.

CLAIMS

1. A process for the joint purification in a wash column by means of a washign liquid of the waste gases and/or vapors formed in the production of inorganic fertilizers, comprising spraying the waste gases introduced into the wash column with a liquid after their entry into a lower part of the wash column.

2. A process according to claim 1, wherein the liquid consists at least partially of the washing liquid used in the wash column.

3. A process according to claim 1 or 2, whrein the amount of spray liquid and the alignment of spray means spraying the spray liquid are selected such that the entering gas stream is completely sprayed.

4. A process according to any one of claims 1 to 3, wherein at least part of the spray liquid is directed against distributor elements of the distributor system for the waste gases.

5. A process according to any one of the preceding claims, wherein the spraying is carried out by nozzles arranged in a distributor system for the waste gases in the wash column.

6. A process according to any one of the preceding claims, wherein droplets of the spray liquid have a diameter of less than 20 μm, preferably of less than 15 μm.

7. A process according to any one of the preceding claims, wherein different waste gas streams of different moisture content are supplied separately.

8. A process according to claim 7, wherein the spraying is directed at the gas stream having the lowest content of water vapor.

9. An apparatus for the joint purification by means of a washing liquid (5) of the waste gases and/or vapors formed in the production of inorganic fertilizers, comprising a wash column (VII) provided with filling means, e.g. packing materials, distributor elements of a gas distributor (IX) for the waste gases to be purified arranged below the filling means in the wash column, and spray nozzles (XIA) for the introduction of wash solution (11) arranged near the said distributor elements (IXA).

10. An apparatus according to claim 9, wherein the spray nozzles (XIA) are directed at the distributor elements (IXA).

11. A process for the joint purification of a washing liquid of the waste gases and/or vapors formed in the production of inorganic fertilizers, the process being substantially as herein described with reference to, and as illustrated in, Figures 1 to 3 of the accompanying drawings.

12. An apparatus for the joint purification of the waste gases and/or vapors formed in the joint production of inorganic fertilizers, the apparatus being constructed and arranged substantially as herein described with reference to, and as illustrated in, Figures 1 to 3 of the accompanying drawings.

Patent Office

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Application No: GB 9715376.1 **Examiner:** Michael R. Wendt
Claims searched: 1 - 12 **Date of search:** 24 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B1R (RAB, RAC, RAD, RAF, RAJM, RM6, RM8)

Int Cl (Ed.6): B01D 53/74, 53/77, 53/78

Other: Online: WPI, Claims, Japio

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0562328 A2	(BASF) - referred to in application - e.g. see Figure 1. Example.	1
X	EP 0440932 A2	(BASF) e.g. see Figure 1. Examples.	1
X	EP 0351613 A2	(BASF) e.g. see Figure 1. Example 1.	1
A	US 5512072	(G. ELECTRIC) e.g. see Figures1 .	1 & 9
X	US 4662929	(KEMIRA) e.g. see Figures 1 - 3. Abstract.	1

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